university of groningen

University Medical Center Groningen

University of Groningen

Luminescent poly(p-phenylenevinylene) hole-transport layers with adjustable solubility

Tanase, C; Wildeman, J; Blom, PWM

Published in:
Advanced Functional Materials

DOI:
10.1002/adfm.200500403

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2005

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
Tanase, C., Wildeman, J., & Blom, PWM. (2005). Luminescent poly(p-phenylenevinylene) hole-transport layers with adjustable solubility. *Advanced Functional Materials*, *15*(12), 2011-2015. https://doi.org/10.1002/adfm.200500403

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license. More information can be found on the University of Groningen website: https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment.

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Download date: 05-05-2023

Luminescent Poly(*p*-phenylenevinylene) Hole-Transport Layers with Adjustable Solubility**

By *Cristina Tanase*, *Jurjen Wildeman*, and *Paul W. M. Blom**

The active part of present polymer light-emitting diodes (PLEDs) consists of only a single layer. Multilayer devices have the advantage that the electron and hole transport can be balanced and that the recombination can be removed from the metallic cathode, leading to higher efficiencies. A major problem for polymer-based multilayer devices is the solubility of the materials used; a multilayer can not be fabricated when a spin-cast layer dissolves in the solvent of the subsequent layer. We demonstrate the development of high-mobility poly(*p*-phenylenevinylene) (PPV)-based hole-transport layers with tunable solubility by chemical modification. Enhanced charge-transport properties are achieved by using symmetrically substituted PPVs; copolymers of long and short side chains enable us to tune the solubility without loss of the enhanced charge transport. Dual-layer PLEDs, in which the holes are efficiently transported via this copolymer towards the luminescent layer, exhibit an enhanced efficiency at high voltages (>10 V) and a strongly improved robustness against electrical breakdown.

1. Introduction

Since the first reports of electroluminescence (EL) in poly(*p*-phenylenevinylene) (PPV),[1,2] light-emitting devices based on conjugated polymers (PLEDs) have become a subject of intense research. It has been recognized that charge transport is an important issue with regard to the performance of these devices.[3–5] From current–voltage measurements it has been demonstrated that the charge transport in single-layer PLEDs is space-charge limited, and that, in addition to transport, the recombination efficiency is also governed by the charge-carrier mobility.[6] Furthermore, due to unbalanced transport between electrons and holes, recombination occurs mainly in a region close to the electron-injecting metal electrode. The quantum efficiency at low bias is reduced as a result of non-radiative energy transfer to the cathode. One way to further optimize the performance of PLEDs is to increase the charge-carrier mobilities of the materials used in them. Such a mobility increase is expected to be accompanied by a decrease in operating voltage, thereby increasing the power efficiency of the PLED. However, in PLEDs based on PPV derivatives with higher mobility, the exciton quenching at the electron-injecting electrode was found to be enhanced, leading to an unexpected decrease in luminescence efficiency.[7] Consequently, the charge-transport properties of the materials presently used in state-of-the-art single-layer PLEDs, with hole mobilities of typically 10^{-11} $m^2 V^{-1} s$, represent the best compromise between these processes. Without the use of high-mobility polymers, low operating voltages are only achieved by keeping the active-layer thickness limited to typically 80–100 nm. This approach makes present-day PLEDs very vulnerable to electrical shorts, and puts strong demands on the processing conditions. These fundamental limitations can be circumvented by using multilayer devices consisting of a number of active layers, each optimized for its own functionality. In a multilayer device, electrons and holes are efficiently transported via high-mobility transport layers towards a highly luminescent layer. As a result, high efficiencies and low operating voltages are simultaneously achieved with relatively thick active layers. This approach has been successfully applied in small-molecule-based devices, in which multiple layers with various functions (charge transport, charge injection, emission) lead to highly efficient devices.[8]

A major problem for polymer-based multilayer devices is the solubility of the materials used; a multilayer cannot be realized when a spin-cast layer dissolves in the solvent of an adjacent layer. In a three-layer device, the luminescent layer has to be cast on top of a hole-transport/electron-blocking layer (HTL/EBL) without dissolving it and, subsequently, an electron-transporting/hole-blocking layer (ETL/HBL) is deposited onto the luminescent layer. As a first approach, efficient bilayer devices have been realized using a precursor PPV as an HTL,[9] which is insoluble after conversion. Another approach to overcome the solubility problem is to crosslink the first (hole-transport) and second (luminescent) layer after deposition. However, the long UV exposure time and reactive end groups needed for crosslinking might strongly decrease the performance of LEDs fabricated from these materials.[10] By using oxetane side groups, it was demonstrated that a light-emitting layer can be crosslinked without loss of luminescence properties.[11] Another recent approach to deposit an ETL on top of luminescent polymers is to make the ETL water soluble.[12] In this way, a bilayer can be fabricated because most of the light-emitting polymers do not dissolve in water. Apart from the sol-

[*] Prof. P. W. M. Blom, C. Tanase, J. Wildeman
Physics of Organic Semiconductors, Materials Science Centre and Dutch Polymer Institute, University of Groningen
Nijenborgh 4, NL-9747 AG Groningen (The Netherlands)
E-mail: P.W.M.Blom@rug.nl

[**] We thank H. F. M. Schoo (TNO) for supplying NRS-PPV and Minte Mulder (RUG) for technical support. This work is part of the research programme of the Dutch Polymer Institute.

 DOI: 10.1002/adfm.200500403 © 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

ubility issue, another important aspect for making efficient polymeric multilayer devices is that the ETL and HTL should have a high mobility in order to minimize the voltage drop across these layers. In the above mentioned approaches, the solubility and charge transport of the HTL, which is the bottom layer of the device, have not been addressed. In this paper, we focus on the development of PPV-based HTLs, which combine an enhanced mobility with a tunable solubility by modification of the chemical structure. First, by altering the unsymmetrical side chains of standard poly(2-methoxy-5-(2′-ethylhexoxy)-*p*-phenylenevinylene) (MEH-PPV) into symmetrical side chains, a mobility increase of two orders of magnitude has been achieved. Subsequently, by introducing an insoluble symmetric polymer unit with short side chains of butyl groups into the chemical structure, the solubility can be tuned without loss of the enhanced charge-transport properties. Using such an HTL, a dual-layer PLED has been fabricated and its performance compared with conventional single-layer PLEDs. It is demonstrated that the dual-layer device is nearly as efficient as a corresponding single-layer device and is by far more robust, withstanding operating voltages twice as large.

2. Results and Discussion

The structures of the polymers studied here are shown in Figure 1 and their syntheses are described in the Experimental section. The devices under investigation consist of a single- or a double-layer polymer sandwiched between a patterned indium tin oxide (ITO) electrode and an evaporated top electrode (see Experimental). The current-density–voltage (*J*–*V*) characteristics of these devices were measured in a nitrogen atmosphere within a temperature range of 190–300 K.

Figure 2 displays a typical example of *J*–*V* characteristics of PPV hole-only diodes performed at room temperature. The current density depends strongly on both the applied bias voltage and the temperature. The analysis of the *J*–*V* measurements with a space-charge-limited (SCL) model[6] provides direct information about the hole mobility. At low electric fields and room temperature, the hole mobility in MEH-PPV amounts to 5×10^{-11} $m^2 V^{-1} s^{-1}$.

Chemical modification of PPV influences the interchain distance, orientation, and packing of the polymer chains and,

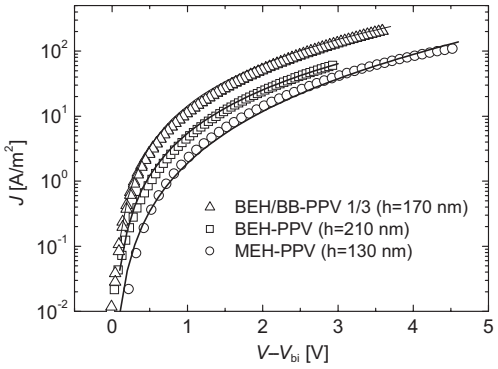

Figure 2. Room-temperature *J*–*V* characteristics of MEH-PPV, BEH-PPV, and BEH/BB-PPV (1:3) hole-only diodes. The applied voltage has been corrected for the built-in voltage (V_{bi}). The solid lines represent the characteristics predicted by the space-charge-limited (SCL) model, including the density-dependent mobility [6].

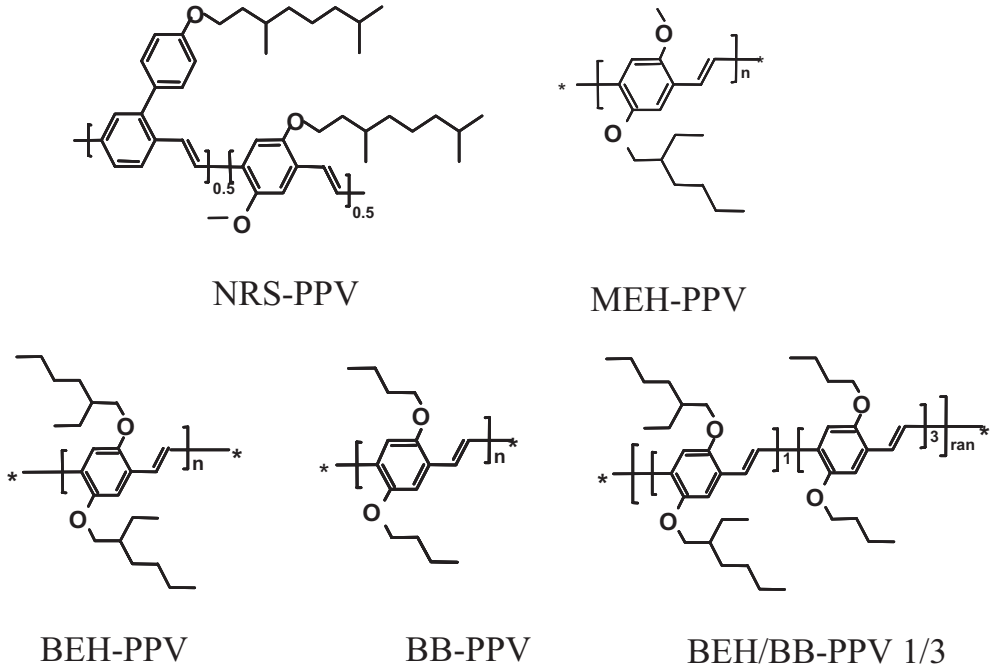

Figure 1. Chemical structures of the polymers. BEH-PPV: poly[2,5-bis(2′-ethylhexyloxy)-1,4-phenylenevinylene]; BB-PPV: poly[2,5-bis(butoxy)-1,4-phenylenevinylene]; NRS-PPV: poly[{2-(4-(3′,7′-dimethyloctyloxyphenyl))}-*co*-{2-methoxy-5-(3′,7′-dimethyloctyloxy)}-1,4-phenylenevinylene].

 © 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

ADVANCED FUNCTIONAL MATERIALS

hence, affects the charge-carrier mobility of the polymer in devices. This has already been demonstrated for OC_1C_{10}-PPV and its derivatives, in which the hole mobility could be varied by over more than two orders of magnitude.[13] The highest mobility, 6×10^{-10} $m^2 V^{-1} s^{-1}$, was achieved in a symmetric $OC_{10}C_{10}$-PPV compound, due to a reduction of the energetic disorder. In this study, we analyze the charge-transport properties of MEH-PPV and several of its derivatives. Following the result in OC_1C_{10}-PPV, we first prepared a symmetric-substituted PPV derivative, namely poly[2,5-bis(2′-ethylhexyloxy)-1,4-phenylenevinylene] (BEH-PPV). The difference between BEH-PPV and MEH-PPV is in the substitution pattern of the side chain: MeO through 2-ethylhexyloxy. Figure 2 also shows the room-temperature *J–V* characteristics of a BEH-PPV hole-only diode. The hole mobility of BEH-PPV amounts to 1.5×10^{-9} $m^2 V^{-1} s^{-1}$, which is 20 times higher than the hole mobility in MEH-PPV. The increase in the mobility in going from MEH-PPV to BEH-PPV is accompanied by a decrease in activation energy, which can be understood in terms of a decrease of energetic disorder determined by the symmetric side chains in BEH-PPV.

From a mobility point of view, BEH-PPV seems to be a good candidate for the transport layer due to its enhanced hole mobility, but its long side chains makes it soluble in many common solvents, such as toluene and chlorobenzene. The solubility can be further reduced by shortening the (2′-ethylhexyloxy) side chains to butoxy side chains. However, poly[2,5-bis(butoxy)-1,4-phenylenevinylene] (BB-PPV) is only soluble in chloroform (see Table 1), and in only very low concentrations. Due to its very poor solubility, diodes can not be fabricated from this material. However, the combination of BEH-PPV and BB-PPV in different ratios in copolymers can induce a variation in solubility, ranging from insoluble in toluene (BB-PPV) to highly soluble in toluene (BEH-PPV), depending on the amount of BB-PPV in the copolymer. The solubility of BEH/BB-PPV in different ratios, 1:*x* (*x* = 1–3), in toluene drops from 0.2 % for BEH/BB-PPV (1:1) to less than 0.1 % for BEH/BB-PPV (1:3). The major question is whether the incorporation of the BB-PPV monomer units affects the enhanced charge-transport properties of BEH-PPV or not. From SCL *J–V* measurements, we find that the hole mobilities of all the copolymers is equal to that of BEH-PPV, 1.5×10^{-9} $m^2 V^{-1} s^{-1}$ at room temperature (see Fig. 2). As a result, BEH/BB-PPV (1:3) combines the desired properties of an HTL in a PLED: high mobility and limited solubility.

A standard material for single-layer PPV-based PLEDs is poly[{2-(4-(3′,7′-dimethyloctyloxyphenyl))}-*co*-{2-methoxy-5-(3′,7′-dimethyloctyloxy)}-1,4-phenylenevinylene] (NRS-PPV).[7] The NRS-PPV used in this study is soluble in a wide range of solvents with a hole mobility of only 1.5×10^{-12} $m^2 V^{-1} s^{-1}$ at low electric fields and room temperature when spin-coated from toluene. A dual-polymer-layer LED can now be constructed using BEH/BB-PPV (1:3) as an HTL and NRS-PPV as an emission layer. The photoluminescence efficiency of NRS-PPV amounts to 20 % and that of BEH/BB-PPV to 9 %, both measured with an integrating sphere.

Table 1. Characteristic properties of the presented polymers. $\mu(E=0)_{RT}$: room-temperature charge-carrier mobility under zero bias; M_w: weight-average molecular weight; M_n: number-average molecular weight.

Polymer	$\mu(E=0)_{RT}$	M_w [g mol^{-1}]	M_n [g mol^{-1}]	Solubility [%]	
				Toluene	Chloroform
NRS-PPV	1.5×10^{-12}	1.0×10^6	1.9×10^5	1	1
MEH-PPV	5.0×10^{-11}	2.1×10^5	6.3×10^4	1	1
BEH-PPV	2.0×10^{-9}	5.5×10^5	1.3×10^5	1	1
BB-PPV	–	–	–	0	0.2
BEH/BB-PPV (1:3)	1.2×10^{-9}	5.7×10^5	4.2×10^5	<0.1	0.6

In Figure 3, the *J–V* characteristics of a single-layer (95 nm thick) NRS-PPV LED, a double-layer BEH/BB-PPV (1:3)/NRS-PPV-based LED together with their light-output characteristics are shown. The thicknesses of the layers in the dual-layer diode are 160 nm for BEH/BB-PPV (1:3) and 95 nm for NRS-PPV. As a reference, the data for a single-layer NRS-PPV-based LED with a thickness comparable to that of the dual-layer device is also shown. When a bias is applied to the diode, the holes are transported efficiently through the BEH/BB-PPV (1:3) and subsequently recombine with electrons in the NRS-PPV layer. It should be noted that the holes can directly enter the NRS-PPV and are not hindered by an energy barrier at the interface, since the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the two polymers align. From Figure 3, it can be observed that, at the same operating voltage, both the current density and the light output of the double-layer device

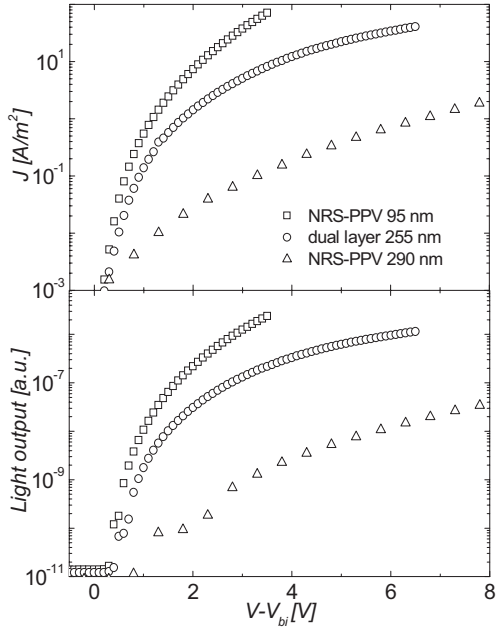

Figure 3. *J–V* characteristics (top) of a single-layer NRS-PPV LED, a dual-layer LED, and a thick NRS-PPV LED with thickness comparable to that of the dual-layer device at room temperature, together with their light-output characteristics (bottom).

 © 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

are significantly smaller than those of the single-layer NRS-PPV diode 95 nm thick. This seems to be in contrast with the large difference in mobility of three orders of magnitude between the BEH/BB-PPV and the NRS-PPV diodes. From device simulations, however, we obtained that the voltage distribution over the two polymers is not governed by the mobility ratio alone. Since the current in the BEH/BB-PPV material is also space-charge limited, a very low voltage drop across this layer directly implies that, electrostatically, only a small amount of charge carriers is allowed in this layer. Therefore, in order to make the HTL highly conductive, a certain voltage drop across this layer is required to fill up the layer with charge carriers. Typically, one third of the voltage drops over the HTL; further details of the device simulations will be published elsewhere.

In Figure 4, the quantum efficiencies (QEs) (ratio of incident photons to charge carriers produced) of the double- and single-layer NRS-PPV devices are shown. The maximum efficiency of the double-layer diode is slightly lower than that of the single-layer NRS-PPV diode. The main reason is that the absorbance and emission spectra of BEH/BB-PPV (1:3) are red-shifted compared to those of NRS-PPV. Therefore, as shown in Figure 5, the absorption spectrum of BEH/BB-PPV slightly overlaps with the emission spectrum of NRS-PPV and part of the generated light is absorbed in the HTL. Consequently, the emission spectrum of the double-layer device is slightly changed; the outer blue part of the emission spectrum of the NRS-PPV in the double layer is cut off.

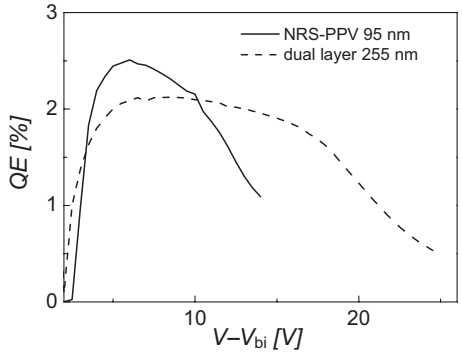

Figure 4. QE as a function of applied bias for NRS-PPV single- and dual-layer LEDs.

Device simulation further demonstrated that the operation of a bilayer device with a large difference in mobility (Fig. 6b) is fundamentally different, compared to a conventional bilayer device in which a mismatch between HOMO and LUMO levels of the two materials has been employed (Fig. 6a).[8,9,14] At the transition from the high-mobility to the low-mobility material, a strong accumulation of holes sets up at the interface, in order to keep the hole current constant across the junction. These accumulated holes pull electrons into the device and, as a consequence, most of the light is generated at the junction, thereby reducing the quenching of electrons at the metallic cathode and enhancing the efficiency. This approach has also recently been applied in bilayers consisting of conjugated dendrimers with tunable mobilities.[15] In this study, the solubility issue has been overcome by vacuum depositing a small-molecule ETL.

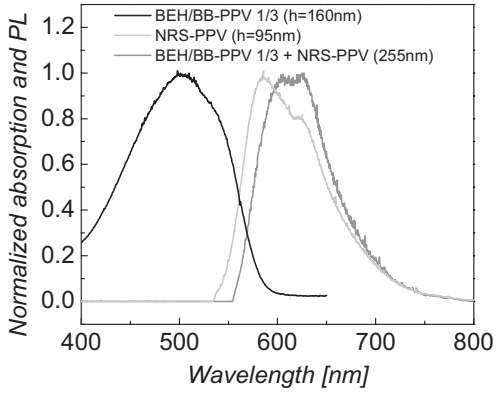

Figure 5. The absorption of BEH/BB-PPV (1:3) and the emission of NRS-PPV and the dual-layer LED.

The double-layer device has a number of advantages over the single-layer PLEDs. The single-layer NRS-PPV LED breaks down around 12–13 V, while the dual layer breaks down at 25–26 V. The reason for this is that, at higher voltages, the field becomes more and more equally distributed over the two polymer layers. At 10 V the efficiency of the two devices is the same, at a typical light output of ~10000 cd m^{-2}. Furthermore, in contrast to conventional HTLs, our HTL is emissive and its HOMO and LUMO levels align with the luminescent layer, so that electrons are not blocked at their interface. Consequently, a short circuit in the luminescent layer does not lead to a catastrophic failure of the device. Instead, the emissive HTL starts to work as an LED and, at the location of the short, only the efficiency of the LED drops since the transport layer is a less-efficient emitter. Additionally, the increased layer thickness of the devices opens the process window of PLEDs in terms of substrate roughness and substrate cleaning. The increased efficiency and lower electric field in the luminescent layer at high voltages, combined with the prevention of catastrophic shorts, are important advantages for the use of PLEDs in passive matrix displays and solid-state lighting applications.

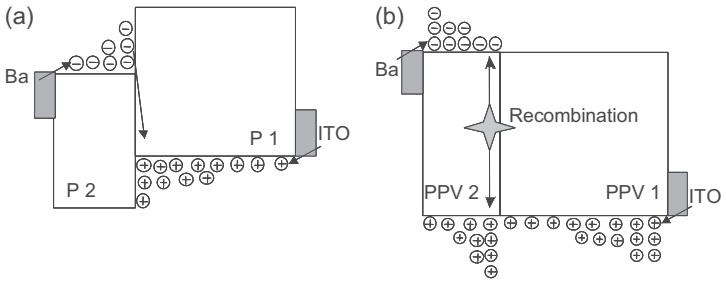

Figure 6. Schematic diagram showing the operation of the dual-layer PLEDs using an energy barrier (a) and mobility transition (b) between the polymers. In both cases the light generation is concentrated at the heterojunction.

 © 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

ADVANCED FUNCTIONAL MATERIALS

In this study, we demonstrate that the application of dual layers is highly beneficial to the processing conditions of PLEDs. As shown in Figure 3, the price paid for a strongly improved processing window is an increase in the operating voltage. However, the desired balance between device thickness and operating voltage is only a matter of tuning the polymer layer thicknesses in the double-layer devices, as shown in Figure 7.

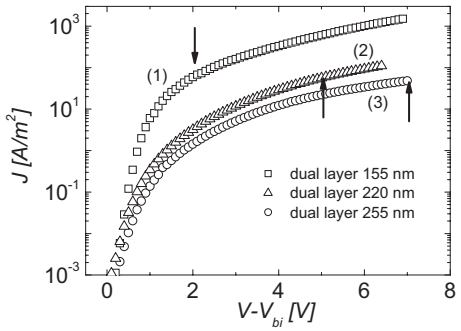

Figure 7. *J–V* characteristics of dual-layer LEDs with different layer thicknesses. The NRS-PPV layer thickness is 75 nm in (1), 85 nm in (2), and 95 nm in (3). The arrows indicate the voltage at which a light output of 100 cd m^{-2} is reached.

The operating voltage of the 100 cd m^{-2} point can be reduced from a $V - V_{bi}$ value of 7.0 to 2.0 V, where the total active-layer thickness still amounts to 155 nm ($V_{bi} = 1.5$ V). For comparison, in the single-layer 95 nm NRS-PPV PLED, 100 cd m^{-2} was reached at $V - V_{bi} = 2.6$ V.

3. Conclusions

In conclusion, it has been demonstrated that the charge-carrier mobilities of PPV-based derivatives can be optimized by chemical modification. Copolymers with selective solubility can be achieved without loss of the enhanced charge-transport properties. Dual-layer PLEDs, in which the holes are efficiently transported via this copolymer towards the luminescent layer, exhibit an enhanced efficiency at high voltages (> 10 V) and a strongly improved robustness against electrical breakdown.

4. Experimental

Polymer Synthesis: MEH-PPV, BEH-PPV, and BEH/BB-PPV (1:3) were synthesized in our laboratory according to the procedure of Neef and Ferraris [16]. The precursors were carefully purified by crystallization (three times) and the obtained polymers were purified by a second precipitation from acetone. Molecular weights were determined by gel-permeation chromatography (GPC); they were measured in trichlorobenzene at 135 °C and calibrated with polystyrene standards. NRS-PPV has been synthesized according to the procedure indicated in a previous publication [17]. In Table 1, the mobilities, molecular weights, and solubilities of the polymers are indicated.

Device Characterization: Prepatterned glass/ITO-substrates were cleaned by ultrasonic treatment in acetone and isopropyl alcohol, and UV-ozone treatment. The polymer layer was spin-coated from a toluene or chloroform solution in a N_2 atmosphere. Finally, an ~ 5 nm Ba layer and an ~ 100 nm Al protecting layer for the LED, and an ~ 80 nm Au layer for the hole-only diode were deposited by thermal evaporation under vacuum (1×10^{-6} mbar; 1 mbar = 100 Pa). The polymer thicknesses were measured using a Dektak profile analyzer. The active area of the devices varied between 7.6 and 99 mm^2. The electrical measurements were done using a Keithley 2400 Sourcemeter in a N_2 atmosphere. The light output was recorded by a calibrated photodiode connected to a Keithley 6514 electrometer. All the measurements were performed within a few hours after the preparation of the samples in order to avoid oxidation of the polymer or the metal.

Received: November 1, 2004
Final version: June 30, 2005
Published online: November 7, 2005

[1] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn, A. B. Holmes, *Nature* **1990**, *347*, 539.
[2] D. Braun, A. J. Heeger, *Appl. Phys. Lett.* **1991**, *58*, 1982.
[3] D. D. C. Bradley, A. R. Brown, P. L. Burn, R. H. Friend, A. B. Holmes, A. Kraft, *Electronic Properties of Polymers*, Springer Solid State Sciences Series, Vol. 107, Springer, Berlin **1992**, p. 304.
[4] A. Kraft, A. C. Grimsdale, A. B. Holmes, *Angew. Chem. Int. Ed.* **1998**, *37*, 402.
[5] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Brédas, M. Lögdlund, W. R. Salaneck, *Nature* **1999**, *397*, 121.
[6] P. W. M. Blom, M. C. J. M. Vissenberg, *Mater. Sci. Eng.* **2000**, *27*, 53.
[7] P. W. M. Blom, M. C. J. M. Vissenberg, J. N. Huiberts, H. C. F. Martens, H. F. M. Schoo, *Appl. Phys. Lett.* **2000**, *77*, 2057.
[8] B. W. D'Andrade, M. A. Baldo, C. Adachi, J. Brooks, M. E. Thompson, S. R. Forrest, *Appl. Phys. Lett.* **2001**, *79*, 1045.
[9] N. C. Greenham, S. C. Moratti, D. D. C. Bradley, R. H. Friend, A. B. Holmes, *Nature* **1993**, *365*, 628.
[10] B. Domercq, R. D. Hreha, Y.-D. Zhang, A. Haldi, S. Barlow, S. R. Marder, B. Kippelen, *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41*, 2726.
[11] C. D. Müller, A. Falcou, N. Reckefuss, M. Rojahn, V. Wiederhirn, P. Rudati, H. Frohne, O. Nuyken, H. Becker, K. Meerholz, *Nature* **2003**, *421*, 829.
[12] W. Ma, P. K. Iyer, X. Gong, B. Liu, D. Moses, G. C. Bazan, A. J. Heeger, *Adv. Mater.* **2005**, *17*, 274.
[13] H. F. C. Martens, P. W. M. Blom, H. F. M. Schoo, *Phys. Rev. B* **2000**, *61*, 7489.
[14] C. W. Tang, S. A. VanSlyke, *Appl. Phys. Lett.* **1987**, *51*, 913.
[15] J. M. Lupton, I. D. W. Samuel, R. Beavington, M. J. Frampton, P. L. Burn, H. Bässler, *Phys. Rev. B* **2001**, *63*, 155 206.
[16] C. J. Neef, J. P. Ferraris, *Macromolecules* **2000**, *33*, 2311.
[17] H. Spreitzer, H. Becker, E. Kluge, W. Kreuder, H. Schenk, R. Demandt, H. Schoo, *Adv. Mater.* **1998**, *10*, 1340.

 © 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim